

Prediction of Multicomponent Adsorption
Equilibria in Background Mixtures of
Unknown Composition

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PREDICTION OF MULTICOMPONENT ADSORPTION EQUILIBRIA IN BACKGROUND MIXTURES OF UNKNOWN COMPOSITION

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Abstract—In the past, most predictive mathematical modeling work has focused on mixtures of known composition. Unfortunately, drinking water and wastewater contain many competing organic solutes and most of them may never be identified. Accordingly, a technique has been developed to predict the adsorption equilibria of known organic solutes onto granular activated carbon (GAC) in mixtures of unknown composition.

Ideal adsorbed solution theory (IAST) was used to describe the competitive interactions between adsorbates. Theoretical components (TCs) were used in IAST calculations to account for the competitive effects of the unknown mixture. The TC isotherm parameters and concentrations were determined by conducting a multicomponent isotherm of a tracer component which is added to the unknown mixture or singled out of the unknown mixture. Once the TC parameters were determined, the identical parameters were used to predict the competitive interactions between any known component and the unknown mixture. This procedure was verified experimentally for two activated carbons, three synthetic mixtures and a contaminated groundwater. The organic solutes were halogenated one and two carbon aliphatics which are common groundwater contaminants.

Key words—multicomponent adsorption equilibria, adsorption equilibria, ideal adsorbed solution theory, activated carbon, volatile organic chemicals

NOMENCLATURE

- C_i = liquid-phase concentration for component i ($M L^{-3}$)
- C_i^s = single solute liquid-phase concentration for component i which is evaluated at the spreading pressure of the mixture ($M L^{-3}$)
- C_{oi} = initial liquid-phase concentration for component i ($M L^{-3}$)
- F_{old} = vector of values of equation (8) which are evaluated at q_{old}
- F_{new} = vector of values of equation (8) which are evaluated at q_{new}
- J = Jacobian of equation (8)
- J^{-1} = inverse of the Jacobian of equation (8)
- K_i = Freundlich capacity parameter for component i ($M M^{-1})(L^3 M^{-1})^{1/n}$)
- m = mass of carbon in isotherm bottle (M)
- N = number of components;
- $1/n_i$ = Freundlich isotherm intensity parameter for component i (dimensionless)
- q_i = solid phase concentration for component i ($M M^{-1}$)
- q_i^s = single solute solid phase concentration for component i which is evaluated at the spreading pressure of the mixture ($M M^{-1}$)
- q_{new} = vector of the new guesses to the roots of equation (8) ($M M^{-1}$)
- q_{old} = vector of the old guesses to the roots of equation (8) ($M M^{-1}$)
- q_T = total surface concentration ($M M^{-1}$)
- V = volume of isotherm bottle (L^3)
- z_i = mol fraction of component i adsorbed on surface (dimensionless).

Abbreviations

- DCE = *cis*-dichloroethene
- EDB = 1,2-dibromoethane
- GAC = granular activated carbon
- IAST = ideal adsorbed solution theory
- LLE = liquid-liquid extraction
- PGAC = powdered granular activated carbon
- RPE = relative percent error as defined in equation (12)
- SOC = synthetic organic chemical
- F^T = transpose of the vector F
- TC = theoretical component
- TCE = trichloroethene
- TOC = total organic carbon
- TOX = total organic halogen
- VOC = volatile organic chemical.

INTRODUCTION

Granular activated carbon (GAC) is a useful technique for removal of some volatile organic chemicals (VOCs) from water and wastewater; however, GAC can be a relatively expensive process. In order to reduce costs, techniques need to be developed to predict process performance so that the cheapest process operation may be selected. With few exceptions, most of the predictive mathematical modeling work has focused on mixtures of known composition (Jossens *et al.*, 1978; Fritz and Schlunder, 1981; Crittenden and Weber, 1978; Crittenden *et al.*, 1980, 1983; Thacker *et al.*, 1983, 1984). Unfortunately,

drinking water and wastewater contain many competing organic solutes. Accordingly, for existing modeling techniques to be applied to actual contaminated waters, it would be necessary to identify and quantify all adsorbing species present. For most applications, this represents an impossible task. Furthermore, even if all the compounds could be identified it would be impossible to solve the resulting model equations that describe their individual behavior.

A technique has been developed to predict multicomponent adsorption equilibria of known VOCs in background mixtures of unknown composition. In addition, this technique was used to simulate the isotherm of total organic halogen (TOX) which has been proposed as a nonspecific measure of organic contamination and may represent a composite isotherm of all the adsorbable chlorinated species. This technique attributes the competitive adsorption equilibrium interactions of the unknown background to theoretical components (TCs). The TC properties were determined, using an adsorbing tracer component, such that the TCs gave the same competitive adsorption effect as the unidentified mixture.

In this study, the unknown background was represented by one or two theoretical components. Calligaris and Tien (1982) and Crittenden *et al.* (1984b) have shown that multicomponent mixtures of VOCs can be grouped into fewer pseudo-species. Hubele and Sontheimer (1983), and Frick and Sontheimer (1983) have used theoretical components to predict adsorption isotherms of total organic carbon (TOC), where each theoretical component represented a portion of the TOC, with the sum of the TC concentrations equalling the TOC concentration. The theoretical component parameters were determined by fitting TOC isotherm profiles. The procedure which is presented herein is similar to the procedure which was proposed by Frick and Sontheimer (1983).

MATERIALS AND METHODS

Chemicals

All chemicals were reagent grade or better. 1,2-Dibromoethane, bromoform, chlorodibromomethane and *cis*-dichloroethene were obtained from Aldrich Chemical Co., Milwaukee, Wis. Methanol, 2,2,4 trimethylpentane, chloroform and trichloroethene were obtained from Burdick and Jackson Co., Muskegon, Mich. Tetrachloroethene and 1,1,1 trichloroethane were obtained from J. T. Baker Chemical Co., Phillipsburg, N.J. Two GACs were used in these studies; Calgon's (Pittsburgh, Pa) Filtrasorb 400 (F-400, lot No. 52095) and Westvaco (Covington, Va) WV-G (lot No. 39815).

Solution preparation

Organic free aqueous ($\text{TOC} < 0.5 \text{ mg l}^{-1}$) solutions were prepared using distilled, deionized Milli-Q water (Millipore Corp., Bedford, Mass.). All experiments were conducted at 10–12°C in a temperature-controlled room. The solutions were buffered with a 0.001 M phosphate buffer at a pH of 6.0.

Chemical analysis

The volatile organic compounds (VOCs) were analyzed using gas chromatography, with liquid-liquid extraction (LLE) and purge and trap methods (U.S.EPA, 1979). The

samples for LLE method were extracted using 5–30 ml solution with 5–10 ml 2,2,4 trimethylpentane following the procedure which was described by Misure (1977). 1,1,1 trichloroethane was used as the internal standard for the LLE method. Hall, electron capture and photoionization detectors were used for identification.

To determine the total organic halogen (TOX) of synthetic mixtures, the GC was used to quantify each halogenated species and the total number of halogens were summed and expressed as chloride. Billets and Lichtenberg (1980) have shown high TOX recovery for many of the solutes which were used in this study would, consequently give similar results to the actual procedure.

Carbon preparation

Representative samples of the GAC were obtained by mixing and splitting the GAC. The GAC which was used in column and rate studies was rinsed with Milli-Q water to remove fines and dried overnight at 105°C.

Powdered granular activated carbon (PGAC), US no. 200 $\times$ 400 sieve was used in the isotherm studies. PGAC was obtained by crushing representative samples of the US no. 12 by 40 sieve carbon such that it all passed the US No. 200 sieve. The PGAC which was retained on a US No. 400 sieve was then cleaned using the same procedure as the GAC.

Isotherm procedure

PGAC was used in the equilibrium studies to reduce the time necessary to reach equilibrium and to insure a representative sample of the carbon was used (Randtke and Snoeyink, 1983; Crittenden *et al.*, 1983). A bottle point isotherm procedure was used to conduct all equilibrium studies. Carbon doses generally ranging from 6 to 3000 mg l^{-1} (1–500 mg in 160 ml bottles) were added to serum bottles that were then filled headspace free with water containing the VOCs. The isotherm bottles were then rotated at 25 rpm and allowed to come to equilibrium.

Once equilibrium was achieved, the PGAC was removed by centrifuging the isotherm bottles and the liquid phase concentrations were determined. In general, 6–7 days were used to equilibrate the PGAC. This was found to be adequate to insure equilibrium in that similar isotherms were found for these solutes that were equilibrated for more than 20 days. The corresponding surface loadings were calculated from this mass balance on an isotherm bottle.

$$q_i = (C_u - C_i) V / M \quad (1)$$

APPROACH

The competitive adsorptive strength of a mixture of unknown components was estimated from the isotherm of a tracer component in that unknown background. The degree to which the tracer component was displaced from its single solute isotherm was used to determine the adsorptive strength of the unidentified background components. This displacement was attributed to theoretical components and their identifying properties were determined by matching the tracer component data in the unidentified background. Ideal adsorbed solution theory (IAST) was used to describe the multicomponent interactions between the tracer component and the unknown background.

The tracer component was either added to the unknown background or singled out of the mixture as being the tracer component. If the tracer component was singled out of the background it was

assumed that it was not a significant portion of the adsorbing components in the mixture.

Local Adsorbed Solution Theory

When all the compounds which are present in a mixture have been identified, IAST can be used to predict the multicomponent equilibria of individual components using single solute isotherm parameters (Radke and Prausnitz, 1972; Jossens *et al.*, 1978; Singer and Chen-Yu, 1980; Okazaki *et al.*, 1980; Fritz and Schlunder, 1981). In another study, Crittenden *et al.* (1984a, 1986) and Luft (1984) demonstrated that IAST could be used to predict multicomponent equilibria for 2, 3 and 6 component mixtures of the compounds which were used in this study.

In IAST, the following five basic equations are used to describe multicomponent behavior:

$$q_T = \sum_{i=1}^N q_i \quad (2)$$

$$z_i = q_i/q_T \text{ for } i = 1 \text{ to } N \quad (3)$$

$$C_i = z_i C_i^o \text{ for } i = 1 \text{ to } N \quad (4)$$

$$1/q_T = \sum_{i=1}^N z_i/q_i \quad (5)$$

$$\int_0^{q_i^o} \frac{d \ln C_i^o}{d \ln q_i^o} dq_i^o = \int_0^{q_i} \frac{d \ln C_i^o}{d \ln q_i^o} dq_i^o \\ = \dots \text{ for } j = 2 \text{ to } N. \quad (6)$$

Equation (2) defines q_T , the total surface loading. Equation (3) defines z_i , the mol fraction of component i on the carbon. Equation (4) is analogous to Raoult's law, where C_i^o is the single solute liquid-phase concentration in equilibrium with q_i^o . The single solute surface loading, q_i^o , is the loading that causes the same spreading pressure, or reduction in surface tension, as the mixture. Equation (5) is the expression for no area change per mol upon mixing from the single solute isotherms at the spreading pressure of the mixture. Equation (6) equates the spreading pressures of the pure component systems to that of the mixture. The integrand in equation (6) is evaluated using the single solute isotherm expression.

If the Freundlich isotherm equation is used to represent single solute behavior, IAST yields the following equation for each adsorbate:

$$C_i = \frac{q_i}{\sum_{j=1}^N q_j} \left[\frac{\sum_{j=1}^N n_j q_j}{n_i K_i} \right]^{1/n_i} \text{ for } i = 1 \text{ to } N \quad (7)$$

in which K_i and $1/n_i$ are the single solute isotherm constants. Equation (7) was combined with the mass balance, equation (1), to eliminate the liquid phase concentration, C_i in IAST predictions for bottle point isotherms as shown in equation (8).

$$F_i(q_1, q_2, \dots, q_N) = C_o - \frac{M}{V} q_i$$

$$- \frac{q_i}{\sum_{j=1}^N q_j} \left[\frac{\sum_{j=1}^N n_j q_j}{n_i K_i} \right]^{1/n_i} \text{ for } i = 1 \text{ to } N. \quad (8)$$

According to equation (8), the equilibrium state in an isotherm bottle may be calculated if the Freundlich K_i , $1/n_i$ and initial concentration of each solute and carbon dose M/V is known. The equilibrium state is given when all the F_i expressions are set equal to zero. Since equation (8) is valid for all components, N nonlinear simultaneous equations with N unknowns must be solved to estimate the final equilibrium state in the isotherm bottle. It is important to recognize that the use of equation (7) assumes that the single solute isotherm may be described by the Freundlich equation over the entire concentration range. Luft (1984) and Crittenden *et al.* (1984a, 1986) have discussed this and other limitations of using equation (7) for equilibrium calculations of mixtures of known components.

This set of equations was solved using a Newton-Raphson algorithm. If we let $\mathbf{q}_{\text{new}}$ equal the new guesses of $[q_1, q_2, \dots, q_N]^T$ (T is the mathematic operand known as the transpose), $\mathbf{F}$ equal $[F_1, F_2, \dots, F_N]^T$ and $\mathbf{J}^{-1}$ equal inverse of the Jacobian of equation (8), the Newton-Raphson algorithm can be formulated by this equation.

$$\mathbf{q}_{\text{new}} = \mathbf{q}_{\text{old}} - \mathbf{J}_{\text{old}}^{-1} \mathbf{F}_{\text{old}} \quad (9)$$

in which, $\mathbf{q}_{\text{new}}$ and $\mathbf{q}_{\text{old}}$ are new and old guesses to the roots of equation (8); $\mathbf{F}_{\text{old}}$ is the numerical value of equation (8) which is evaluated at $\mathbf{q}_{\text{old}}$. The off diagonal elements of the Jacobian are given by:

$$\frac{\partial F_i(q)}{\partial q_k} = \frac{q_i}{\left[\sum_{j=1}^N q_j \right]^2} \left[\frac{\sum_{j=1}^N n_j q_j}{n_i K_i} \right]^{1/n_i} \\ - \left[\frac{q_i n_i}{\sum_{j=1}^N q_j} \right] \left[\frac{\sum_{j=1}^N n_j q_j}{n_i K_i} \right]^{1/n_i - 1} \quad (10)$$

[Equation (10) is valid for all i and k except when k equals i .] And the diagonal elements of the Jacobian are [equation (11) is valid only when i is equal to k]:

$$\frac{\partial F_i(q)}{\partial q_i} = -\frac{M}{V} - \frac{1}{\sum_{j=1}^N q_j} \left[\frac{\sum_{j=1}^N n_j q_j}{n_i K_i} \right]^{1/n_i} \\ + \left[\frac{q_i}{\sum_{j=1}^N q_j} \right] \left[\frac{\sum_{j=1}^N n_j q_j}{n_i K_i} \right]^{1/n_i} \\ - \left[\frac{q_i n_i^2}{\sum_{j=1}^N q_j} \right] \left[\frac{\sum_{j=1}^N n_j q_j}{n_i K_i} \right]^{1/n_i - 1} \quad (11)$$

To implement this algorithm, we start with a initial guess for q and improve our guess using equations (9)–(11) until equation (8) is satisfied. This usually took 4–6 iterations.

Prediction of multicomponent equilibria of unknown mixtures using theoretical components to represent the unknown mixture in IAST calculations

According to equation (8), these three parameters are needed to characterize the adsorptive strength of each TC: initial concentration, C_0 , Freundlich K , and $1/n$. These parameters were determined by fitting both the liquid and solid phase isotherm data for the tracer component in the mixture using the relative % error (RPE) as defined in this equation:

$$RPE = \frac{100}{N} \sum \left[\frac{|X_{\text{observed}} - X_{\text{predicted}}|}{X_{\text{observed}}} \right] \quad (12)$$

Accordingly, 3 parameters were fit for each theoretical component that was used to represent the adsorption strength of the background.

Theoretical components were also used to predict a total surrogate parameter, TOX. TOX was simulated by summing the total TC molar concentrations which are obtained from the tracer fit, and multiplying by three as shown in this equation.

TOX concentration

$$= \sum (\text{theoretical component concentrations}) \times 3. \quad (13)$$

Equation (13) assumes that each TC contains three halogens per molecule. This requires that the total initial concentration of the theoretical components must equal one-third of the initial TOX concentration. For the case where a TOX isotherm is fit simultaneously with the tracer isotherm, equations (8) and (13) must be satisfied simultaneously. This will reduce the number of parameters that need to be fit by one. In that case, the parameter which was no longer determined by fitting the data was the initial concentration of one of the TCs. As shown in Figs 1–3, the TC parameters are strongly correlated; consequently, it would not significantly change the results if other values were assumed for the number of halogens on the TCs or the number of parameters are reduced by one.

RESULTS AND DISCUSSION

Equilibrium studies

The theoretical component procedure was applied to three synthetic mixtures and a contaminated groundwater. The three synthetic mixtures were made up of 6 components. Although individual measurements of the components were made, only the TC properties were used to predict the competitive interactions between the synthetic mixture and an individual component. For the synthetic mixtures, one component was singled out as the tracer component and

the reduction in its capacity as compared to its single solute capacity was used to determine the TC properties. Once the TC properties were known, the competitive interactions between the synthetic mixture and any individual component in the mixture was predicted by using the TC properties in IAST calculations. Accordingly, the synthetic mixtures are unknown mixtures with respect to equilibrium calculations because the initial concentrations and isotherm parameters of all the components that make up the mixture were not used in the calculations.

The procedure which was applied to a contaminated groundwater was similar to the one which was applied to the synthetic mixtures. One component of the groundwater was singled out as the tracer component and the TC properties were determined by fitting the isotherm of the tracer component. However, in this case, the concentration of the tracer was increased over its naturally-occurring level to facilitate its measurement. Once the TC properties of the contaminated groundwater were identified, they were used to predict the competitive interactions between another component which was present in the groundwater. The concentration of the other component which was present in the contaminated groundwater was also increased to facilitate its measurement.

Accordingly, to predict the competitive interactions between an unidentified mixture and any individual component. A single solute and mixture isotherm for the tracer are required to determine the TC properties. The TCs properties and a single solute isotherm of any individual component are all that is needed to predict competitive interactions between the mixture and that individual component. More details and all raw isotherm data were reported by Luft (1984).

Sensitivity analysis

A sensitivity analysis was performed on the TC parameters to assess their relative impact on the IAST calculations that use TCs to represent the unknown mixture. Table 1 lists the initial concentrations of the three synthetic mixtures that were used to test the TC approach. For mixture III, only one TC was required to fit the tracer component data; consequently, a sensitivity analysis was performed on this mixture. The TC properties for Mixture III are given in Table 2. Each TC parameter, K , $1/n$ and C_0 , was individually changed $\pm 50\%$. The resulting IAST calculations for chlorodibromomethane which was the tracer component are presented in Figs 1–3. The single solute isotherm which is plotted as a dashed line is also shown for comparison. Both $1/n$ and C_0 had significant impact on the predicted results.

These results show that the effect of any one parameter may not be separated from the effects of the other parameters; therefore, the TC parameters are cross correlated and more than one set of TC parameters may be used to describe the competitive

Table 1. Initial concentrations of the six components which are present in the three synthetic mixtures

Component	Mixture I ($\mu\text{M l}^{-1}$)	Mixture II ($\mu\text{M l}^{-1}$)	Mixture III ($\mu\text{M l}^{-1}$)
Chloroform	14.04	4.0	17.3
Chlorodibromomethane	12.41	4.0	15.1
1,2-Dibromomethane	13.41	3.6	20.3
Bromoform	11.94	3.7	22.1
Trichloroethene	13.52	3.3	13.4
Tetrachloroethene	12.29	2.9	6.5

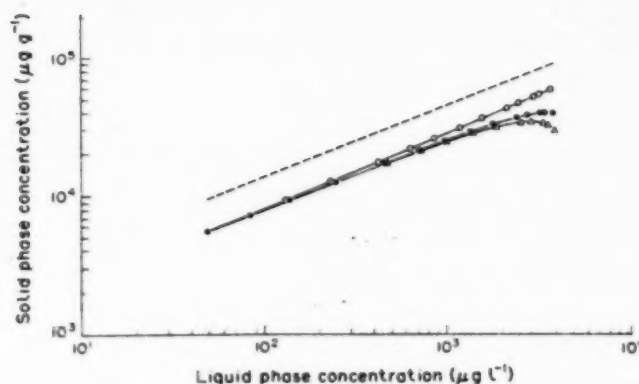


Fig. 1. The effect of changing the theoretical component Freundlich K by $\pm 50\%$ on the ideal adsorbed solution theory calculations of chlorodibromomethane equilibria in Mixture III. — Represent single solute data; $\bullet$ represent best fit; Δ represent $+50\%$ in K ; $\circ$ represent -50% in K . Laboratory parameters: pH = 6.0; carbon type F-400; equilibrium time = 6 days; temperature = 10°C ; particle diameter $200 > D > 400$ mesh.

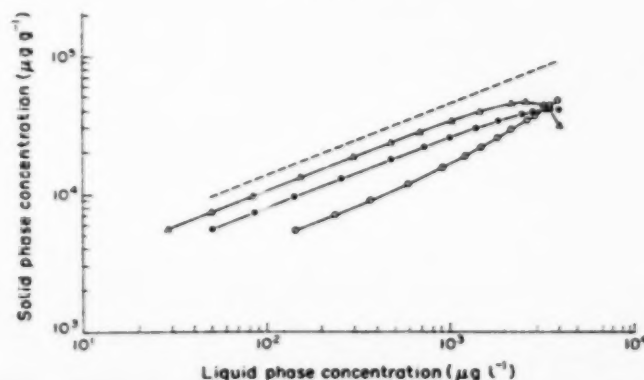


Fig. 2. The effect of changing the theoretical component Freundlich $1/n$ by $\pm 50\%$ on the ideal adsorbed solution theory calculations of chlorodibromomethane equilibria in Mixture III. — Represent single solute data; $\bullet$ represent best fit; Δ represent $+50\%$ in $1/n$; $\circ$ represent -50% in $1/n$. Laboratory parameters as Fig. 1.

interactions with the background. In this work, the number of TCs that were used to represent the adsorptive strength of the unknown mixture was determined by the RPE of the fit. The TC parameter search algorithm continued to increase the number of TCs until the RPE did not decrease by using more TCs. This was one or two TCs in the four mixtures which were studied.

Single solute isotherm tests

Single solute isotherm experiments were conducted to determine isotherm parameters for use in IAST calculations using TCs to represent the adsorption strength of the unknown mixture. Each single solute data set was fit with the Freundlich isotherm equation:

$$q_i = K C_i^{1/n} \quad (14)$$

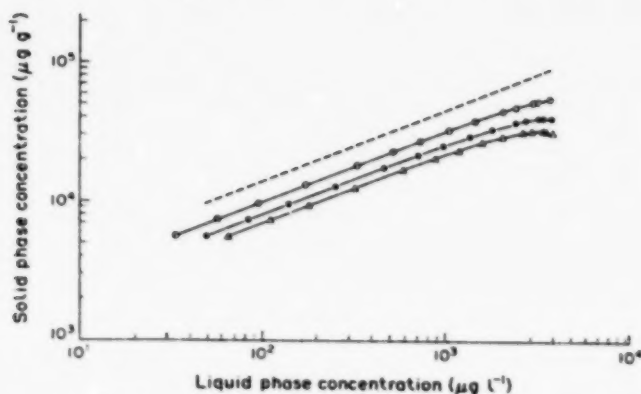


Fig. 3. The effect of changing the theoretical component initial concentration by $\pm 50\%$ on the ideal adsorbed solution theory calculations of chlorodibromomethane equilibria in Mixture III. --- Represent single solute data; $\bullet$ represent best fit; Δ represent $+50\%$ in C_0 ; $\circ$ represent -50% in C_0 . Laboratory parameters as Fig. 1.

The best set of isotherm data was obtained for 1,2-dibromoethane and its was described with excellent precision by the Freundlich isotherm with an RPE of 3.9% in C and 1.1% in q . The isotherm data for trichloroethene had the most scatter of the single solute isotherms with an RPE of 14.9% in C and 1.5% in q . The isotherm parameters were determined by a linear least squares regression of the logs of the C and q data. The single solute isotherm parameters along with 95% confidence bands on K and $1/n$ are given in Table 3.

Predicting total organic halogen and specific compounds with theoretical components

For Mixtures I and II, both the tracer data (chlorodibromomethane) for Mixture I and the TOX data were fit to determine the TCs properties which are reported in Table 2. Two TCs were required to fit the ClBr_2CH and TOX data. Figures 4-6 show the fit to the ClBr_2CH data and the prediction of 1,2-dibromoethane (EDB) and trichloroethene (TCE) data using the theoretical component parameters for Mixture I. The data are represented by solid circles

Table 2. Theoretical component properties for Mixtures I, II and III and the relative % error of the fits and predictions of the data

Compound	Best fit or prediction	Mixture	Relative % error C	Relative % error q	Number of data points
Chlorodibromomethane	Fit	Mixture I	13.6	5.9	25
Chloroform	Pred.	Mixture I	10.1	26.6	24
Trichloroethene	Pred.	Mixture I	22.7	3.2	25
1,2-Dibromomethane	Pred.	Mixture I	14.0	6.1	25
Bromoform	Pred.	Mixture I	19.2	10.0	24
Tetrachloroethene	Pred.	Mixture I	51.5	1.9	15
Chloroform	Pred.	Mixture II	19.4	33.1	17
Trichloroethene	Pred.	Mixture II	21.7	4.3	15
Chlorodibromomethane	Pred.	Mixture II	22.3	9.7	19
1,2-Dibromoethane	Pred.	Mixture II	21.6	7.2	17
Bromoform	Pred.	Mixture II	56.8	4.7	15
Tetrachloroethene	Pred.	Mixture II	80.7	4.3	9
Chlorodibromomethane	Fit	Mixture III	13.8	2.3	14
Chloroform	Pred.	Mixture III	3.7	12.1	14
Trichloroethene	Pred.	Mixture III	11.7	2.3	10
1,2-Dibromoethane	Pred.	Mixture III	18.8	2.2	13
Bromoform	Pred.	Mixture III	21.5	14.5	9
Tetrachloroethene	Pred.	Mixture III	32.9	2.3	7

Theoretical Component Properties for Mixtures I and II

$K(\mu\text{M g}^{-1})(\mu\text{M l}^{-1})^{1/n}$	$1/n$	Mixture I $C_0(\mu\text{M l}^{-1})$	Mixture II (25% of Mixture I) $C_0(\mu\text{M l}^{-1})$
73.1	0.6902	67.09	18.79
15913.0	0.4777	10.15	2.84

Theoretical Component Properties for Mixture III

$K(\mu\text{M g}^{-1})(\mu\text{M l}^{-1})^{1/n}$	$1/n$	$C_0(\mu\text{M l}^{-1})$
81.0	0.7212	89.41

Table 3. Summary of the single component isotherms, experimental conditions and Freundlich isotherm parameters

Carbon type, size, temperature water matrix	Compound	Equilibration time (days)	95% Confidence interval			95% Confidence interval			Concentration range ($\mu\text{g l}^{-1}$)
			K (μM^{-1}) best fit	$1/n$ best fit	K	$1/n$ best fit	K	$1/n$ best fit	
F-400 200 by 400 Mesh 9-11°C Milli-Q water	<i>cis</i> -Dichloroethene	7.0	151	0.151	120-190	20-57	0.7045	0.6687-0.7402	120-1250
	Trichloroethene	6.5	1390	0.1390	2800-4100	120-310	0.4163	0.3620-0.4706	5.6-360
	Tetrachloroethene	6.0	10,400	0.10400	9400-11400	530-800	0.4579	0.4365-0.4794	3.5-1170
	Bromodiform	10.0	1800	0.1800	1700-1900	180-180	0.5629	0.5528-0.5730	40.0-2000
	Chloroform	7.0	284	0.284	250-320	24-38	0.5325	0.5102-0.5549	8.0-1180
WV-G 200 by 400 Mesh 9-11°C Milli-Q water	1, 2-Dibromomethane	7.0	1790	0.1790	1600-1800	98-142	0.4808	0.4637-0.4979	32.0-1750
	chlorodibromomethane	7.0	1270	0.1270	980-1600	60-150	0.5170	0.4758-0.5581	92.0-1820
	<i>cis</i> -Dichloroethene	7.0	180	0.180	140-240	23-57	0.6441	0.6045-0.6383	143-1340
	Trichloroethene	6.5	3260	0.3260	3000-3600	150-220	0.4073	0.3850-0.4295	5.3-120
	Tetrachloroethene	3.0	2850	0.2850	2500-3300	110-210	0.3944	0.3561-0.4327	3.7-400
		6.0	7520	0.7520	6700-8400	460-750	0.5017	0.4762-0.5271	7.0-910

Note: all the above isotherms were conducted at a pH of 6.0.

and the predictions are represented by open boxes. In cases where the prediction agrees exactly with the data, the solid circles hide the predictions.

The displacement of the EDB, TCE, $\text{C1Br}_2\text{CH}$ isotherms from their single solute values can be seen by comparing the mixture data (solid circles) to the single solute isotherms which are represented by the dashed lines. This displacement is the greatest for higher liquid-phase concentrations (or for small PGAC doses) because the competitive interactions are greater due to the higher surface loadings of the strongly adsorbing components.

For the theoretical component approach to be generally applicable, it was necessary to demonstrate that the identical TCs may be used to predict background competition when the background is concentrated or diluted. As shown in Table 1, a second six component mixture isotherm, Mixture II, was conducted at about 28% of the initial concentrations of Mixture I. The compounds in Mixture II were predicted using the TCs determined from $\text{C1Br}_2\text{CH}$ in Mixture I. The initial concentrations of the TCs were decreased by 28% to correspond to the amount of dilution from Mixture I. [Note the total mixture concentrations for Mixtures I and II are related to the total TOX by equation (13); therefore, the TOX concentration is not equal to the total mixture concentration.] The results for $\text{C1Br}_2\text{CH}$, EDB and TCE are shown in Figs 7-9. The displacement of the isotherms from their single solute values can be seen by comparing the data (solid circles) to the single solute isotherms, represented by the dashed lines.

In order to apply the procedure, an important condition must be met for the components which are predicted using the TC parameters. That is, it must be demonstrated that the predicted components are a small part of the adsorption strength of the mixture, because its adsorption potential is already accounted

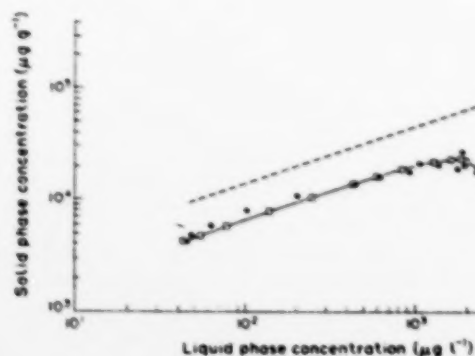


Fig. 4. Chlorodibromomethane isotherm data in multicomponent Mixture I, the fit of the data using two theoretical components (the TOX data for Mixture I was fit simultaneously) and the single solute isotherm. --- Represent single solute data; ● represent mixture data; □ represent model fit. Laboratory parameters as Fig. 1.

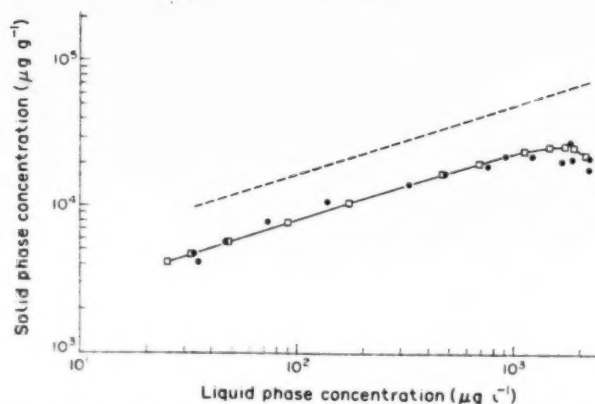


Fig. 5. 1,2-Dibromoethane isotherm data in multicomponent mixture I, the prediction of the data using two theoretical components (which were determined by fitting the chlorodibromomethane and TOX isotherm data in mixture I) and the single solute isotherm. --- Represent single solute data; ● represent mixture data; □ represent model predictions. Laboratory parameters as Fig. 1.

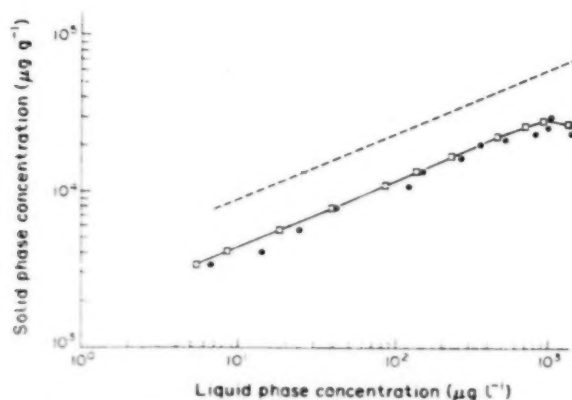


Fig. 6. Trichloroethene isotherm data in multicomponent Mixture I, the predictions of the data using two theoretical components (which were determined by fitting the chlorodibromomethane and TOX isotherm data in Mixture I) and the single solute isotherm. --- Represent single solute data; ● represent mixture data; □ represent model predictions. Laboratory parameters as Fig. 1.

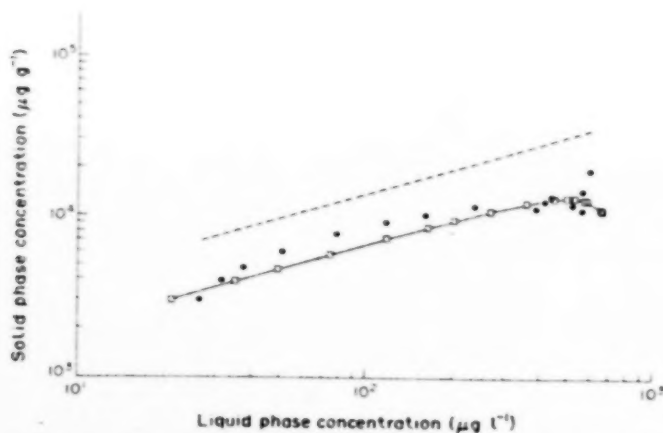


Fig. 7. Chlorodibromomethane isotherm data in multicomponent Mixture II, the predictions using two theoretical components (which were determined by fitting the chlorodibromomethane and TOX isotherm data in Mixture I) and the single solute isotherm. --- Represent single solute data; ● represent mixture data; □ represent model predictions. Laboratory parameters as Fig. 1.

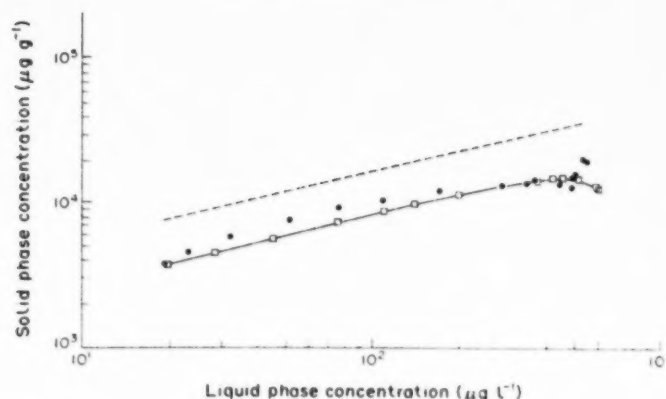


Fig. 8. 1,2-Dibromoethane isotherm data in multicomponent Mixture II, the prediction using two theoretical components (which were determined by fitting the chlorodibromomethane and TOX isotherm data in Mixture I) and the single solute isotherm. --- Represent single solute data; ● represent mixture data; □ represent model predictions. Laboratory parameters as Fig. 1.

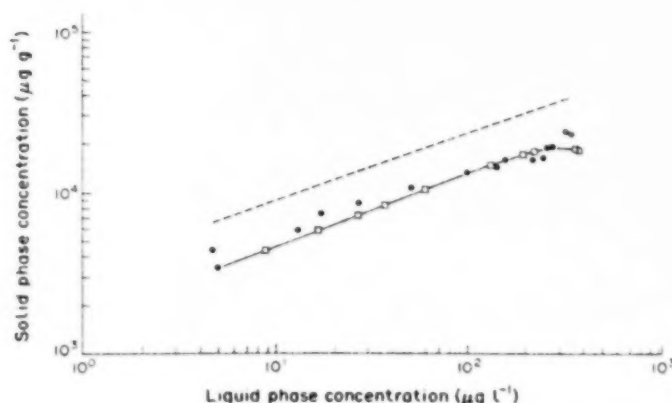


Fig. 9. Trichloroethene data in multicomponent Mixture II, the prediction using two theoretical components (which were determined by fitting the chlorodibromomethane and TOX isotherm data in Mixture I) and the single solute isotherm. --- Represent single solute data; ● represent mixture data; □ represent model predictions. Laboratory parameters as Fig. 1.

for in the IAST calculations by the TC parameters. If this condition is not met, the IAST predictions for these components would yield a lower capacity than is observed. This condition is met for Mixture I because the total adsorption potential of the TCs which is represented by their Freundlich K_s and the initial concentrations (see Table 2) is much greater than that of the predicted components. (See Tables 1-3 for C_{∞} , K and $1/n$ values.) Accordingly, the concentrations of the predicted components did not represent a significant portion of the competitive adsorption interactions in the original mixture.

Figure 4 shows the TC fit to the chlorodibromomethane data. Figures 5-9 provide a visual comparison between TC predictions for Mixtures I

and II. Table 2 provides a complete comparison between all the data for Mixtures I and II. As indicated in Table 2, there are 11 TC predictions and the average percent errors between the predictions and data demonstrated that the TCs approach give excellent predictions. Figure 10 displays the TOX data for both Mixtures I and II, and TC fit of Mixture I data and the TC prediction of Mixture II. As shown in Fig. 10, the fit of the TOX data for Mixture I is excellent as shown by the open boxes that are covered up by the TOX data which is represented by solid boxes. However, the TOX data for Mixture II which are represented by solid circles were not described by the TC predictions as shown by open circles. The reason it did not predict the

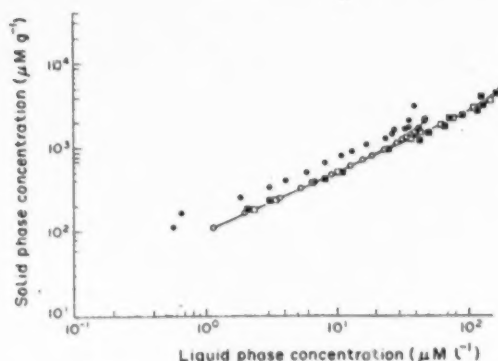


Fig. 10. Total organic halogen isotherm fit for Mixture I (the chlorodibromomethane data in mixture was fit simultaneously) and the prediction of total organic halogen isotherm for Mixture II using two theoretical components. ■ Represent Mixture I isotherm data; □ represent Mixture I isotherm fit; ● represent Mixture II data; ○ represent Mixture II predictions. Laboratory parameters as Fig. 1.

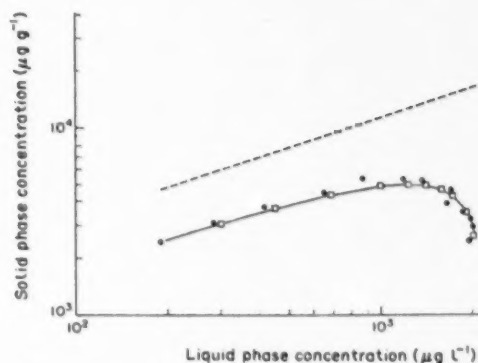


Fig. 11. Chloroform isotherm data in Mixture III, the prediction using one theoretical component (which was determined by fitting the chlorodibromomethane and TOX data in Mixture III) and the single solute isotherm. --- Represent single solute data; ● represent mixture data; □ represent model predictions. Laboratory parameters as Fig. 1.

results for Mixture II is that one of the theoretical components had a much greater capacity than the other as shown in Table 2. Accordingly, at high PGAC doses or low liquid phase concentrations, the TOX prediction converged to the single solute value for the strongly adsorbing TC. To predict the TOX isotherm in the diluted mixture, Mixture II, it would be necessary to have a large amount of curvature in the TOX data of Mixture I. This would allow for the determination of more than one significantly adsorbing theoretical component.

Theoretical component modeling was also applied to Isotherm III, another six component isotherm. Once again, chlorodibromomethane was used as the tracer and both the tracer data and TOX was fit simultaneously to determine the TC. For Mixture III, one TC was found to be sufficient to fit the ClBr_2CH and TOX data. The TC parameters are given in Table 2. Figure 11 shows the prediction of the chloroform data using the TC and Table 2 reports the RPE between the data and TC predictions. Once again the agreement between the TC predictions and the data were good.

Theoretical component procedure applied to a contaminated groundwater

The theoretical component procedure was applied to isotherms conducted in an actual contaminated groundwater which was obtained from a contaminated well in a Midwestern city. An analysis of the VOCs and total organic carbon that were found in the water are reported in Table 4. The VOCs did not account for all the organics in the background as the TOC concentration was 8.4 mg l^{-1} . Two compounds, TCE and *cis*-dichloroethene (DCE), and two carbons (F-400 and WV-G) were used to verify the procedure. For all four isotherms in the con-

taminated groundwater, the concentration was increased to about 8 μM l^{-1} for the compound being measured.

For the TCE and DCE isotherms which were conducted on a given carbon, the DCE isotherm data was first fit to determine the TC properties and then the TCE isotherm data was predicted using those TC properties and visa versa. Table 5 reports two such predictions for each of the two carbons for a total of 4 TC predictions. The resulting TC properties and RPE of the fits and predictions are all reported in Table 5. It is evident there is a lack of consistency in the TC properties for the mixture using TCE and DCE as tracers; however, the sensitivity analysis (see Figs 1-3) showed that it would be difficult to obtain one unique set of TC parameters. However, the calculated displacement of the tracer component from its single isotherm was nearly identical for the TC fit or TC prediction using TC parameters that were determined from another tracer.

As in the case for the predictions for Mixtures I-III, it must be demonstrated that the predicted component does represent a significant part of the adsorption strength of the mixture which are represented by the TCs. This condition is met for this contaminated groundwater because the adsorption potential of the mixture which is represented by the Freundlich K_s and the initial concentrations of the

Table 4. Analysis of contaminated groundwater

Component	Concentration
<i>cis</i> -Dichloroethene	213.2 μg l^{-1}
Trichloroethene	193.5 μg l^{-1}
Tetrachloroethene	128.8 μg l^{-1}
Toluene	59.1 μg l^{-1}
Xylene	20.8 μg l^{-1}
<i>o</i> and <i>p</i> -Xylene	29.5 μg l^{-1}
Total organic carbon	8.4 mg l^{-1}

Table 5. Theoretical components (TC) parameters and relative % errors between TC fits and predictions for *cis*-dichloroethene in the contaminated groundwater

Compound	Best fit or prediction	Carbon type	K (μMg^{-1})($1\mu\text{M}^{-1}$) ^{1/n}	Components $1/n$	C_e (μMl^{-1})	Relative % error C	Q	Number of data points
<i>cis</i> -Dichloroethene	Fit	F-400	709.2	0.503	5.4	8.8	17.4	15
			1133.6	0.559	10.0			
Trichloroethene	Pred.	F-400				113.2	19.1	17
Trichloroethene	Fit	F-400	440.9	0.333	5.6	21.3	1.8	17
			19660.0	1.000	0.26			
<i>cis</i> -Dichloroethene	Pred.	F-400				9.8	36.3	15
<i>cis</i> -Dichloroethene	Fit	WV-G	259.5	0.338	6.5	9.3	15.5	15
			0.57	0.997	132.9			
Trichloroethene	Pred.	WV-G				34.6	2.7	16
Trichloroethene	Fit	WV-G	783.1	0.416	7.5	38.7	0.9	16
			18100.0	0.894	13.8			
<i>cis</i> -Dichloroethene	Pred.	WV-G				9.0	18.6	15

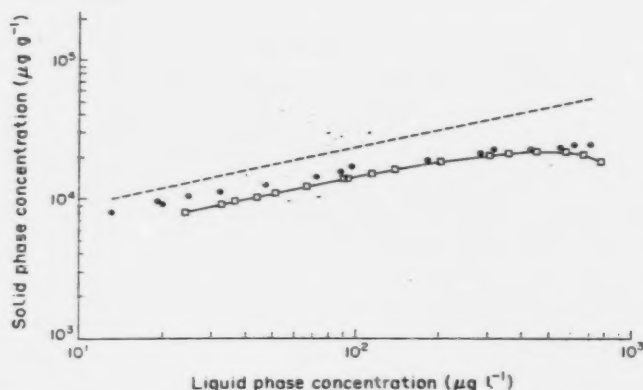


Fig. 12. Isotherm data for trichloroethene for F-400 carbon in the presence of a contaminated groundwater, the prediction of the data using two theoretical components (which were determined by fitting the *cis*-dichloroethane data) and the single solute isotherm. ● Represent experimental data; — represent single solute data; □ represent model predictions. Laboratory parameters: Contaminated groundwater was obtained on 20 February 1984; pH = 6.2; carbon type F-400; temperature = 10°C; equilibrium time = 6 days; particle diameter 200 < D < 400 mesh.

theoretical components (see Table 5), is much greater than that of the predicted components in the original mixture. (See Tables 3 and 4 for original concentrations in the mixture and the isotherm parameters.) Accordingly, the original concentrations of the predicted components did not represent a significant portion of the competitive adsorption interactions in the original mixture. As a general strategy, a weakly adsorbing component should be used as the tracer component so that the TCs would represent nearly all of the adsorption strength of the mixture.

Figure 12 shows the prediction of the TCE isotherm for F-400 carbon using theoretical components fit to DCE, while Fig. 13 shows the prediction of DCE for WV-G carbon using theoretical components fit to TCE. These two predictions represent the worst and the best predictions. The RPEs of the fits and predictions in Table 5 demonstrated that the TCs adequately predicted the component that was not fit.

CONCLUSIONS

Equilibrium competitive interactions between individual components and unknown mixtures can be

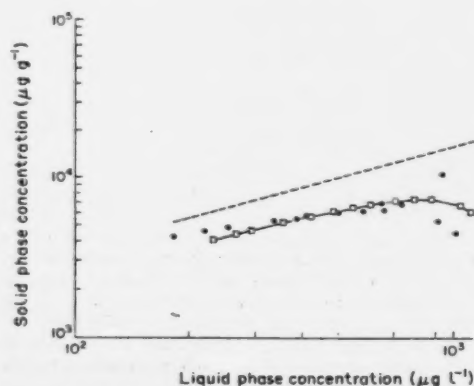


Fig. 13. Isotherm data for *cis*-dichloroethene for WV-G carbon in the presence of a contaminated groundwater, the prediction of the data using two theoretical components (which were determined by fitting the trichloroethene data) and the single solute isotherm. ● Represent experimental data; — represent single solute data; □ represent model predictions. Laboratory parameters: Contaminated groundwater obtained on 20 February 1984; pH = 6.2; carbon type WV-G; temperature = 10°C; equilibrium time = 6 days; particle diameter 200 < D < 400 mesh.

described using theoretical components to represent the background strength. Simple isotherm tests using an adsorbing tracer can be used to estimate the theoretical properties. Equilibrium competitive interactions were described with a previously unreported simple form of the IAST. Both mixtures of similar size molecules and an actual contaminated groundwater were used to verify the procedure. In all, there were 20 successfully predicted isotherms using this procedure involving 321 data. Two activated carbons and 7 organic solutes were involved in the study. However, the theoretical component procedure was only tested extensively for molecules which are similar in nature and more testing is required for dissimilar molecules. (The procedure was validated for an actual groundwater that contained dissimilar molecules.) In addition, column testing is required to check the isotherm capacity which was predicted using theoretical components. Surrogate isotherms such as TOX can be correlated to theoretical components but they were not predicted for higher or lower strengths of the unknown mixture.

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REFERENCES

- Billets S. and Lichtenberg J. J. (1980) Total organic halide method 450.1. Environmental and Monitoring Support Laboratory, Cincinnati, Ohio.
- Calligaris M. B. and Tien C. (1982) Species grouping in multicomponent adsorption calculations. *Can. J. Engng.* **60**, 772-780.
- Crittenden J. C. and Hand D. W. (1983) Design considerations for the removal of synthetic organic chemicals and THM precursors using granular activated carbon. Proceedings of a Seminar, *Strategies for Controlling Trihalomethanes*. American Water Works Association.
- Crittenden J. C. and Weber W. J. Jr (1978) Model for design of multicomponent adsorption systems. *J. env. Engng Div. Am. Soc. civ. Engrs* **104**, No. EE6, 1175-1195.
- Crittenden J. C., Luft P. J. and Hand D. W. (1984a) Multicomponent adsorption of volatile organic chemicals onto granular activated carbon. *Proceedings of the 1984 National American Water Works Association Meeting*, Dallas, Tex.
- Crittenden J. C., Wong B. W. C., Thacker W. E., Snoeyink V. L. and Hinrichs R. L. (1980) Mathematical model of sequential loading in fixed-bed adsorbers. *J. Wat. Pollut. Control Fed.* **52**, 2780.
- Crittenden J. C., Loper S., Luft P. J., Hand D. W., Oravitz J. and Ari M. (1984b) Multicomponent adsorption of volatile organic halogen in competing background mixtures of unknown composition. *Proceedings of the 1984 National Conference on Environmental Engineering*, Sponsored by ASCE, Los Angeles, Calif.
- Crittenden J. C., Loper S., Luft P. J., Hand D. W., Oravitz J. and Ari M. (1986) Multicomponent adsorption of volatile organic chemicals onto granular activated carbon. *J. env. Sci. Technol.* In press.
- Frick B. R. and Sontheimer H. (1983) In *Treatment of Water by Granular Activated Carbon*, pp. 247-268. American Chemical Society Books, Washington, D.C.
- Fritz W. and Schlunder E. U. (1981) Competitive adsorption of two dissolved organics onto activated carbon. *Chem. Engng Sci.* **36**, 721-730.
- Hubele C. and Sontheimer H. (1983) Isotherm evaluation and filter breakthrough calculations for waters with a multicomponent mixture of organics, using the simplified competitive adsorption model (SCAM). University of Karlsruhe, Federal Republic of Germany.
- Jossens L., Prausnitz J. M., Fritz W., Schlunder E. U. and Myers A. L. *Chem. Engng Sci.* **33**, 1097-1106.
- Luft P. J. (1984) Modeling of multicomponent adsorption onto granular carbon in mixtures of known and unknown composition. Submitted in partial fulfillment of a Master of Science degree in Chemical Engineering, Michigan Technological University, Houghton, University Microfilms, Ann Arbor.
- Mieure J. P. (1977) A rapid and sensitive method for determining volatile organohalides in drinking water. *J. Am. Wat. Wks Ass.* **69**, 60-62.
- Okazaki M., Hiroyuki K. and Toie R. (1980) Prediction of liquid phase adsorption equilibria of multisolute in water. *J. chem. Engng Japan* **13**, 286-291.
- Radke C. J. and Prausnitz J. M. (1972) Thermodynamics of multisolute adsorption from dilute liquid solutions. *AIChE JI* **18**, 761.
- Randtke S. J. and Snoeyink V. L. (1983) Evaluation of GAC adsorptive capacity. *J. Am. Wat. Wks Ass.* **75**, 406-413.
- Singer P. C. and Chen-Yu (1980) Adsorption of alkyl phenols by activated carbon. *Activated Carbon Adsorption*, Vol. 1. Ann Arbor Science, Ann Arbor Mich.
- Thacker W. E., Crittenden J. C. and Snoeyink V. L. and (1984) Modeling of adsorber performance: variable influent concentration and comparison of adsorbents. *J. Wat. Pollut. Control. Fed.* **56**, 243-250.
- Thacker W. E., Snoeyink V. L. and Crittenden J. C. (1983) Desorption of compounds during operation of GAC adsorption systems. *J. Am. Wat. Wks Ass.* **75**, 144.
- U.S. EPA (1979) The analysis of trihalomethanes in finished water by the purge and trap method. U.S., Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

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